

Formulation and baking process affect Maillard reaction development and antioxidant capacity of ginger cakes

HENRYK ZIELIŃSKI – MIRYAM AMIGO-BENAVENT –
MARIA DOLORES DEL CASTILLO – ANNA HORSZWALD – DANUTA ZIELIŃSKA

Summary

Four different types of ginger cakes, two according to the traditional making process and two others according to the new recipes, were baked at 180 °C for 18 min. Ginger cakes formulated according to the new recipe (mixed wheat/rye flours) showed lower antioxidant capacity by 70% than traditional cakes formulated on dark or brown rye flour. The traditional ginger cakes were a better source of extractable phenolics than the newly formulated ones. The average contents of extractable total phenolic compounds in traditional ginger cakes were about 48% higher compared to those found in new ones. The formulation and making process improved antioxidant properties of ginger cakes and generated a significant amount of Maillard reaction products. Application of new recipes improved nutritional quality of ginger cakes due to a higher protein quantity and lesser contents of components potentially harmful to human health. Based on the higher protein quality and chemical data, ginger cakes formulated according to new recipes should be preferred with the aim to lower the intake of dietary advanced glycation end products.

Keywords

ginger cake; total phenolics; antioxidant capacity; Maillard reaction products

Ginger cake is a typical traditional food, originally a favourite treat throughout Europe including Russia, Lithuania, Estonia and Poland. Similar to bread baking, ginger cake became a matter of pride for many communities. The most popular bakeries of ginger cakes were in Nuremberg (Germany), Toruń (Poland), Tula and Arkhangelsk (Russia). Ginger cake remains fresh and tasty for a long time. The cake may be stored in a dry and cold place up to about two months. Dark rye flour (100% extraction rate) and brown rye flour (90% extraction rate) are mostly employed for traditional ginger cake making. However, mixtures of wheat and rye flours have recently begun to be employed for the cake making. The traditional ginger cake recipe includes other ingredients such as milk, caramelized sugar, honey, cinnamon and ginger, while additional eggs are included in the new recipe of ginger cake.

Recently, we reported the higher falling number as well as protein and minerals in dark rye flour than in brown rye flour (extraction rate of 90%). Moreover, dark rye flour showed a higher content of bioactive compounds (total phenolic compounds, total flavonoids, inositol hexaphosphate, tocopherols and tocotrienols) when compared to the brown flour [1]. The typical taste of ginger cakes originates from their ingredients, mainly from cinnamon, ginger and honey. The antioxidant properties of these ingredients have already been well documented. Cinnamon contains flavonoids, mainly glycoflavonols, possessing free radical-scavenging properties [2]. Ginger antioxidant capacity has been ascribed to the presence of gingerol-related compounds and diarylheptanoids [3]. Honey has been reported to be rich in polyphenol antioxidants [4, 5]. Moreover, sugar caramelization products have also been described as power-

Henryk Zieliński, Anna Horszwald, Division of Food Science, Institute of Animal Reproduction and Food Research of Polish Academy of Sciences, Tuwima 10, P. O. Box 55, 10-718 Olsztyn 5, Poland.

Miryam Amigo-Benavent, Maria Dolores del Castillo, Instituto de Fermentaciones Industriales (CSIC), C/Juan de la Cierva 3, 28006 Madrid, Spain.

Danuta Zielińska, Department of Chemistry, University of Warmia and Mazury in Olsztyn, Plac Lodzki 4, 10-957 Olsztyn, Poland.

Correspondence author:

Henryk Zieliński, tel.: +48-89-523-46-82; fax: +48-89-524-01-24; e-mail: h.zielinski@pan.olsztyn.pl

ful antioxidant compounds [6]. Eggs are a primary source of high-quality proteins and additionally offer antioxidants, such as vitamin E, A, B₁₂ and B₂, selenium and a substantial amount of lutein [7]. Moreover, eggs contain two proteins, phosvitin and conalbumin, and relatively high levels (7%) of lecithin that have been reported to display antioxidant properties [8].

During baking, many chemical events occur that induce modifications in the chemical composition and properties of food [9–12]. It is believed that Maillard reaction or simply food component degradation induced by heating may affect the chemical composition and consequently the antioxidant capacity of ginger cake [11, 13]. Moreover, Maillard reaction products generated at advanced reaction stage, called food-derived advanced glycation end products (food-AGE), have been reported to be toxic and were proposed to be causative factors for various kinds of diseases, in particular diabetes and kidney disorder, through the association with receptor of AGE (RAGE). It has also been reported that food-derived AGE may not be a causative factor for prooxidation. However, the relationship of food-AGE and biological AGE is not clear [14].

To the best of our knowledge, no information related to the antioxidant capacity of ginger cakes, including neo-antioxidants formed during baking, has been published until now. The aim of the present study was to find out how the formulation and baking conditions affect antioxidant capacity and Maillard reaction development in ginger cakes made following traditional and new recipes. Results obtained may help to improve the ginger cake making process in order to produce a healthier food.

MATERIALS AND METHODS

Chemicals

Furosine (2-furoylmethyl-lysine) was from NeoMPS (Strasbourg, France). Methanol (HPLC-grade) and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were from Merck (Darmstadt, Germany). Other chemicals were of reagent quality grade and were provided by POCh (Gliwice, Poland). Deionized water was purified with a MilliQ system (Millipore, Bedford, Massachusetts, United States).

Flours and ginger cake-making process

Rye grains cv. Warko were obtained from a local plant breeding station in Poland. Dark and brown flours with extraction rates of 100% and

Tab. 1. The formulation of ginger cakes.

Ingredient [g]	Traditional recipe		New recipe	
	Type 1	Type 2	Type 3	Type 4
Dark rye flour	500	0	200	0
Brown rye flour	0	500	0	200
White wheat flour	0	0	300	300
Honey	200	200	200	200
Sugar	250	250	250	250
Egg	0	0	40	40
Sodium bicarbonate	15	15	15	15
Ginger spice	40	40	40	40

90%, respectively, were obtained using Quadrumat Senior equipment (Brabender, Duisburg, Germany). White wheat flour, floral honey and sugar were purchased at a local market in Olsztyn, Poland. Fresh eggs, properly stored, originated from a local market in Olsztyn. They were used before the recommended use-before date stated on the retail package, which was in accordance with the current 30-day industry-standard shelf-life.

Four different cakes were made, two being based on single rye flours and two based on mixtures of rye and white wheat flours. Formulation of the cakes is shown in Tab. 1. Ginger cakes of type 1 and 2 were made following the traditional recipe, while the other two cakes, type 3 and 4, were prepared according to the procedure currently employed in the new recipe. The traditional ginger cake-making process involved dough preparation by mixing flour, honey and sugar (without eggs), and storage at 20–22 °C for 5 days. Afterwards, sodium bicarbonate and ginger spices were added. The dough was cut into 0.5 cm thick discs of 5.5 cm diameter and were baked at 180 °C for 18 min in a DC-32E electric oven (Sveba-Dahlen, Fristad, Sweden). At least 20 units of each type of ginger cakes were made. Ginger doughs and cakes were freeze-dried and ground. The powdered samples were sieved through a 60-mesh screen and stored at –20 °C until analysed.

Sample preparation

Powdered samples (175 mg) were mixed with 6.25 ml of 75 mmol·l⁻¹ phosphate buffer (pH 7.4), incubated at room temperature for 60 min at stirring every 15 min for 30 s and filtered through a paper filter Whatman No. 40 (Whatman, Maidstone, United Kingdom). The filtrates were employed for analysis of total extractable phenolics, antioxidant capacity and advanced Maillard reaction products.

Determination of total extractable phenolic compounds (extractable TPC)

Extractable TPC were assayed according to SINGLETON et al. [15]. Briefly, 0.25 ml of 0.75 mmol·l⁻¹ phosphate buffer filtrates were mixed with 0.25 ml of Folin-Ciocalteu reagent/water (1:1 v/v), 0.5 ml of saturated sodium carbonate and 4 ml of water. The mixture was incubated at a room temperature for 25 min and centrifuged at 2000×g for 10 min. Absorbance of the clear supernatants was measured at 725 nm using a spectrophotometer UV-160 1PC (Shimadzu, Kyoto, Japan). The content of the extractable phenolic compounds in each sample was calculated by employing a standard curve prepared using ferulic acid and expressed as grams of ferulic acid equivalents (FAE) per kg of dry matter (DM). Analyses were carried out in triplicate.

Determination of the antioxidant capacity by cyclic voltammetry (CV) method

A potentiostat/galvanostat (Gamry, Warminster, Pennsylvania, United States) was used for voltammetric experiments [16]. Measurements were performed with extracts (28 g·l⁻¹) mixed with 75 mmol·l⁻¹ phosphate buffer (pH 7.4). The voltammetric experiments were carried out at a room temperature using apparatus cell (volume 200 μl), to which extracts mixed with the buffer solution were introduced. One hundred μl of each extract and 100 μl of 75 mmol·l⁻¹ phosphate buffer solution were used in the assays. The cyclic voltammograms were acquired in the range of -100 mV to +1300 mV at a scanning rate of 100 mV·s⁻¹ at 2 mV intervals, and the total charge was measured below the anodic wave curve of the voltammogram. Trolox was dissolved in 75 mmol·l⁻¹ phosphate buffer (pH 7.4) and then was mixed with 75 mmol·l⁻¹ phosphate buffer (pH 7.4) at a ratio of 1:1 (v/v). The cyclic voltammograms were acquired in the range of -100 mV to +1300 mV at a scanning rate of 100 mV·s⁻¹ at 2 mV intervals. The total charge below the anodic wave of 75 mmol·l⁻¹ phosphate buffer solutions of Trolox within the concentration range of 0.025–0.50 mmol·l⁻¹ was used for standard curve construction and was applied to determine the antioxidant capacity as mmol·kg⁻¹ DM (expressed as Trolox equivalent). The total charge under the anodic wave of the background signal (solvent + supporting electrode) was subtracted from the total charge under the anodic wave obtained for each sample measured within the range from +100 mV to +1200 mV. Triplicate samples were run for each set.

Measurement of Maillard reaction development

Furosine assay

Formation of early Maillard reaction products (MRP) was indirectly measured as furosine analysis by capillary zone electrophoresis (CZE). Prior to the CZE analysis, the samples were prepared according to the procedure described by RESMINI et al. [17]. An accurately weighted powdered sample containing 40–50 mg of protein was hydrolysed with 8 ml of 8 mol·l⁻¹ HCl at 110°C for 23 h under anaerobic conditions. The hydrolysate was filtered through Whatman No. 40 filter paper and the filtrate (0.5 ml) was cleaned up employing a Sep-pak C₁₈ cartridge (Waters, Tauton, Massachusetts, United States), and pre-treated with 5 ml of methanol and 10 ml of deionized water. The CZE method was based on that of DELGADO-ANDRADE et al. [18]. For separation, a G1600A capillary electrophoresis instrument equipped with a ChemStation software was used (Agilent, Palo Alto, California, USA). CZE was performed on uncoated fused silica capillary 48.5 cm long (40 cm to the detector) with an internal diameter of 50 μm and a 3× bubble cell. Other conditions of analyses were as follows: buffer, 50 mmol·l⁻¹ sodium phosphate, pH 7.0; voltage, 25 kV; temperature of analysis, 25 °C; injection for 4 s at 500 kPa; electroosmotic flow marker, acetone. Electrophoregrams were monitored at 280 nm and the spectra collected from 190 nm to 600 nm. The capillary was conditioned after each sample run by flushing at 500 kPa for 12 s with 0.1 mol·l⁻¹ NaOH and for 24 s with 0.05 mol·l⁻¹ sodium phosphate (pH 7.0). Identity of the furosine peak was confirmed on the basis of migration time, furosine standard addition and spectral analysis. The linear response of furosine within the content of 5–100 mg·kg⁻¹ was used for standard curve construction ($y = 0.486x - 0.386$; $R^2 = 0.99$) and it was applied to quantify furosine in the samples. Data were the mean values ($n = 2$) expressed as g·kg⁻¹ protein. Protein content was measured following the AOAC method, and nitrogen-to-protein conversion factor used was 6.25 [19].

Measurement of MRP fluorescence and calculation of the FAST index

The FAST method (Fluorescence of Advanced Maillard Products and Soluble Tryptophan) is based on the determination of maximal fluorescence emission when exciting at 330–365 nm, which corresponds to molecular structures formed between reducing saccharides or oxidizing lipids and lysine residues of proteins. This fluorescence is dependent on heat treatment and related to pro-

tein nutritional loss. Applied to a soluble extract of the food and corrected for the protein concentration of the solution obtained, using tryptophan fluorescence, the method allows to calculate the FAST index as an indicator of the nutritional damage during heat process. Therefore, FAST index comprises fluorescence of advanced MRP and soluble tryptophan. MRP fluorescence is related to free fluorescent intermediary compounds formed at the advanced stage of Maillard reaction.

Filtrates prepared previously for determination of extractable phenolics and antioxidant capacity were further employed for determination of the FAST index as reported by BIRLOUEZ-ARAGON et al. [20]:

$$\text{FAST index} = 100 \times [FIC / Trp_{FL}] \quad (1)$$

where *FIC* is fluorescence of free fluorescent intermediary compounds measured at excitation wavelength $\lambda_{ex} = 363$ nm and emission wavelength $\lambda_{em} = 431$ nm, while *Trp_{FL}* means tryptophan fluorescence at $\lambda_{ex} = 290$ nm and $\lambda_{em} = 340$ nm. Readings were recorded in an RF-1501 spectrofluorimeter (Shimadzu) setting the slit width at 2.5 nm. The samples were analysed in triplicate and FAST index data were expressed in % (w/w).

Brown pigments assay

Formation of brown pigments was estimated in filtrates as absorbance at 420 nm [21]. The assay was performed in a Coulter DU 800 spectrophotometer (Beckman Instruments, Fullerton, California, United States). All measurements were made in triplicate. Results were expressed as arbitrary absorbance units.

Statistical analysis

Results of the chemical analyses are given as mean values and the standard deviation of three independent measurements. Data were subjected to a one-way analysis of variance (ANOVA) using the Fischer LSD test with the Statgraphic 5.0 Program (Statistical Graphic, Rockville, Maryland, United States). The programme was employed for statistical analysis of the data with the level of significance set at 95%. The correlation analysis was performed and the Pearson correlation coefficient was calculated.

RESULTS AND DISCUSSION

Total extractable phenolic compounds content

The content of total extractable phenolic compounds (TPC) in ginger doughs and cakes is shown in Tab.2. The average content of extractable TPC

in the samples based on single rye flour (types 1 and 2) was by about 48% higher compared to that found in the samples elaborated by mixing white wheat and rye flours (types 3 and 4). Data suggest that traditional ginger cakes formulated with dark or brown rye flours (types 1 and 2) may be better sources of extractable TPC than the cakes made following the new recipe (types 3 and 4). Moreover, the thermal processing caused a statistically significant increase in the phosphate buffer-extractable TPC in both traditional and new formulated cakes. Baking improved physical accessibility of TPC enhancing their extractability. The increase in TPC by 54% and 92%, respectively, was noted in the traditional ginger cakes (types 1 and 2, respectively), whereas in ginger cakes of type 3 and 4, respectively, formulated based on mixed wheat/rye flours, it was of 66% and 44%, respectively. This finding clearly confirmed our previous results indicating higher contents of phenolic compounds in dark and brown rye flours than in white wheat flour [22]. Therefore, replacement of 60% of the respective rye flour with white wheat flour in the formulations and baking may modify the content of extractable TPC. This is in accordance with the previously reported profile of phenolic acids in traditional rye breads based on the dark and rye brown flours [20]. Phenolic acids are mainly localized in the outer part of cereal grains. For example, ferulic acid in rye grain is the most abundant phenolic compound present in bran [23].

Tab. 2. Contents of the total extractable phenolic compounds (TPC) and antioxidant capacities of ginger doughs and cakes.

Dough/cake		TPC [g·kg ⁻¹]	Antioxidant capacity [mmol·kg ⁻¹]
Type 1	Dough	2.45 ± 0.12 ^a	1.22 ± 0.47 ^a
	Cake	3.78 ± 0.17 ^{bA}	1.59 ± 0.39 ^{aAB}
Type 2	Dough	2.31 ± 0.09 ^a	1.64 ± 0.23 ^a
	Cake	4.44 ± 0.21 ^{bB}	2.13 ± 0.10 ^{bB}
Type 3	Dough	1.60 ± 0.11 ^a	1.05 ± 0.41 ^a
	Cake	2.65 ± 0.14 ^{bC}	0.97 ± 0.06 ^{aA}
Type 4	Dough	1.62 ± 0.06 ^a	1.03 ± 0.04 ^a
	Cake	2.33 ± 0.14 ^{bC}	1.21 ± 0.11 ^{aA}

Values are means ± standard deviation (*n* = 3). Values in each column for each type of ginger dough and cake with different superscript small letters are significantly different (*p* ≤ 0.05). Values in each column followed for ginger cakes with different capital superscript letters are significantly different (*p* ≤ 0.05).

TPC is expressed in grams of ferulic acid equivalents per kg of dry matter. Antioxidant capacity is expressed in mmol of Trolox equivalents per kg of dry matter.

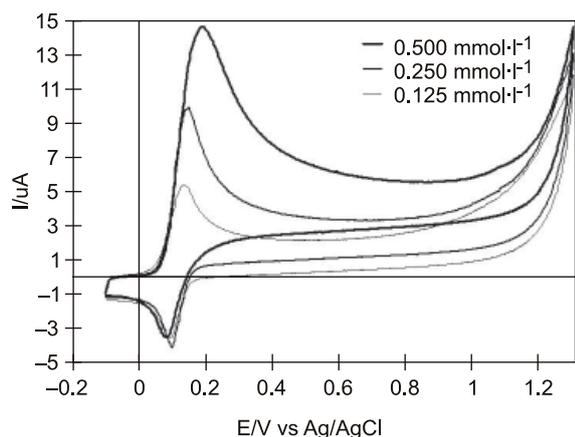


Fig. 1. Cyclic voltammograms of selected Trolox concentration vs. the total charge under the anodic wave.

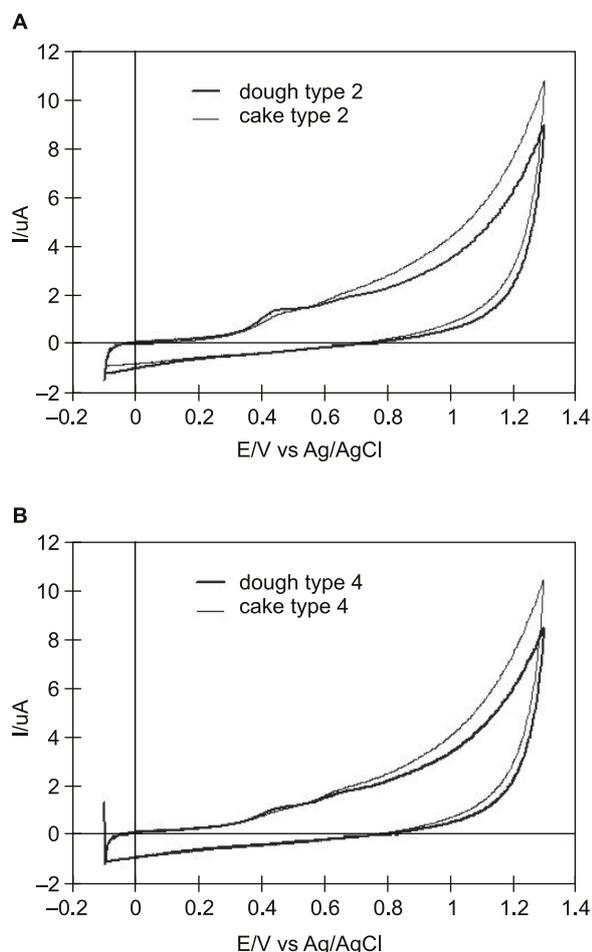


Fig. 2. Cyclic voltammograms of 75 mmol·l⁻¹ phosphate buffer extracts (pH 7.4) from (A) ginger doughs and cakes of type 2, (B) doughs and cakes of type 4. Please see table 1 for details of the formulation of ginger cake of type 2 and of type 4.

Antioxidant capacity of ginger cakes evaluated by cyclic voltammetry

A cyclic voltammogram (CV tracing) provides information describing the integrated antioxidant capacity without the specific determination of the contribution of each individual component. It is based on the analysis of the anodic current waveform, which is a function of the reductive potential of a given compound in the sample and/or a mixture of components. The total antioxidant capacity of the sample is a function combining two sets of parameters. The first is the biological oxidation potential, whereas the second is the intensity of the anodic current waveform, reflecting the concentration of the components. Recently, it has proposed that the area under the anodic current wave (S ; related to the total charge) is a better parameter reflecting the antioxidant capacity of the sample [16]. Therefore, the cyclic voltammetry method used in this study was based on the correlation between the total charge below anodic wave of cyclic voltammograms and the antioxidant capacity of the sample and reference substance (Trolox).

The cyclic voltammograms of selected Trolox concentrations (0.05–0.50 mmol·l⁻¹) were recorded for constructing a calibration curve ($y = 128.85x + 3.32$; $R^2 = 0.99$), which was then employed for quantification of the antioxidant capacity of the samples. Voltammograms obtained for the standard solutions of Trolox showed well-resolved peaks and a shoulder in the potential region up to 1.1 V. A typical CV tracing of different Trolox concentrations is shown on Fig. 1. The representative voltammograms obtained for ginger dough and cake of single brown rye flour products (type 2) and white wheat/brown rye mixed flour products (type 4) are shown in Fig. 2. The observed anodic wave was broadened due to the response of several antioxidants with different oxidation potentials [3–5, 24–27]. The antioxidant capacity of traditional and newly-formulated ginger doughs ranged from 1.64 ± 0.23 mmol·kg⁻¹ to 1.03 ± 0.04 mmol·kg⁻¹ (expressed as Trolox equivalent on DM basis; Tab. 2). No significant changes in the antioxidant capacity were observed at baking of dough named as type 1, type 3 and type 4. The baking of the dough type 2 caused a slight but statistically significant increase in the antioxidant capacity measured by the CV assay.

MRP generated during ginger cake making process

Tab. 3 shows data on protein and Maillard reaction products generated from that macromolecule through the most relevant chemical

event taking place during the baking process. Products formed during the three main stages of this complex network of reactions (Maillard reaction) are summarized in the Tab. 3 as furosine – early product, fluorescent intermediary compounds or advanced glycation end products (AGE) and browning – polymers generated at the very last stage of this reaction. Products formulated according to the traditional recipe showed lower protein values than those prepared following the new recipe based on egg addition due to the contribution of egg protein. Protein content of pasteurized eggs has recently been reported as $473 \pm 5.8 \text{ g} \cdot \text{kg}^{-1}$ DM, whilst that of lysine as $69.9 \pm 2.9 \text{ g} \cdot \text{kg}^{-1}$ of protein [28]. It was in agreement with the level of 6.24% of available lysine reported in egg albumin by Boctor and Harper [29]. Baking decreased the protein content of cakes within the range of 5–12%, showing the highest decrease in ginger cakes made by employing the new recipe (type 3 and 4, respectively).

Significant formation of MRP was observed in all types of ginger cakes (Tab. 3). Furosine offers the advantages of being a direct marker of lysine reaction products, which are not only of analytical and technological but also of nutritional relevance. It is a representative marker of Amadori products from the early stage of the Maillard reaction that are nutritionally unavailable [30]. Furosine was detected in dough taken directly before baking. The doughs of type 1 and type 2 contained almost seven times less furosine than those of type 3 and type 4. Moreover, furosine content of 75 commercial shell egg samples ranged from

$0.1 \text{ g} \cdot \text{kg}^{-1}$ to $0.8 \text{ g} \cdot \text{kg}^{-1}$ of protein, and its concentration was stable during storage at 20°C [31], showing only the natural variation [32]. Therefore, differences in furosine value can be explained on the basis of the protein composition of the cakes (Tab. 1) taking into account the contribution of egg albumin to the formation of furosine during dough storage at a room temperature [28]. Moreover, the protein composition of white wheat flour may also contribute to the higher level of furosine noted in dough type 3 and type 4 prepared with a new recipe.

Baking caused a significant increase in furosine in all types of ginger cakes. However, the real increase of the furosine contents after baking, calculated as differences in its content in dough and cake of each type, were almost the same irrespective of the cakes formula. The average value from the differences between furosine content in dough and cake of each type was $5.04 \pm 0.48 \text{ g} \cdot \text{kg}^{-1}$ of protein. This finding clearly indicated the high extent of Maillard reaction during ginger cake baking as about four-five times lower furosine levels have been reported in various thermally-processed cereal foods like dried pasta [33], cookies, crackers, breakfast cereals [18, 34], baby cereals and commercial breads [11, 35].

The tryptophan fluorescence noted in dough of type 1 (55.1 ± 3.4) was slightly higher than that corresponding to dough of type 2 (42.6 ± 2.7 ; Tab. 3). In contrast, tryptophan fluorescence noted in ginger dough of type 3 and 4 was almost two-three fold higher, indicating the contribution of this amino acid from egg albumin [29]. Fluorescence

Tab. 3. Data on protein, furosine, tryptophan fluorescence, fluorescent advanced MRP, FAST index and development of browning in ginger doughs and cakes.

Dough/cake		Protein [g·kg ⁻¹]	Tryptophan fluorescence	Early MRP	Advanced MRP	Final MRP
				Furosine [mg·kg ⁻¹]	FAST index	Browning
Type 1	Dough	68.1 ± 1.6^a	55.1 ± 3.4^a	927 ± 74^a	42.8 ± 0.9^a	0.18 ± 0.01^a
	Cake	64.8 ± 0.3^{aA}	2.0 ± 0.1^{bA}	6585 ± 305^{bA}	2772.9 ± 83.9^{bA}	0.30 ± 0.02^{bA}
Type 2	Dough	66.6 ± 0.9^a	42.6 ± 2.7^a	835 ± 116^a	88.5 ± 6.6^a	0.18 ± 0.01^a
	Cake	63.6 ± 0.9^{aA}	2.4 ± 0.1^{bA}	5537 ± 28^{bA}	2092.2 ± 164.2^{bB}	0.28 ± 0.01^{bA}
Type 3	Dough	119.9 ± 2.1^a	115.5 ± 1.2^a	6660 ± 88^a	28.9 ± 0.7^a	0.21 ± 0.01^a
	Cake	105.7 ± 1.4^{bB}	14.6 ± 1.3^{bB}	11846 ± 255^{bB}	299.1 ± 38.5^{bC}	0.27 ± 0.01^{bA}
Type 4	Dough	107.7 ± 0.1^a	202.8 ± 0.3^a	4968 ± 65^a	15.8 ± 0.1^a	0.20 ± 0.04^a
	Cake	94.3 ± 1.9^{bC}	21.3 ± 1.6^{bC}	9573 ± 621^{bC}	213.6 ± 11.3^{bC}	0.24 ± 0.02^{aA}

Values are means \pm standard deviation ($n = 3$). Values in each column for each type of ginger dough and cake with different small superscript letters are significantly different ($p \leq 0.05$). Values in each column for ginger cakes with different capital superscript letters are significantly different ($p \leq 0.05$).

Tryptophan fluorescence is expressed in fluorescence arbitrary units. FAST index data are expressed in percent. Browning is expressed as arbitrary absorbance units.

due to tryptophan of all cakes was drastically decreased by the baking process (from 10 to around 30 times). The remaining tryptophan fluorescence in ginger cakes formulated following the new recipe (type 3 and 4) was about 10 times higher than that found in traditional cakes.

Tab. 3 shows also the FAST index results. This parameter is a ratio between fluorescence of advanced MPR (*FIC*) and fluorescence due to the soluble tryptophan [36]. In agreement with furosine values, a significant increase in FAST index was caused by baking independently on the food composition (Tab. 3). Interestingly, values found in cakes made according to the traditional recipe showed FAST index values approximately 10 fold higher than those prepared following the new recipe. This finding seems to indicate that ginger cakes made following the new recipe may have better nutritional quality and be healthier than those made according to the traditional recipe. Dietary advanced MPR may play a role in causing of chronic diseases associated with underlying inflammation, and their excessive consumption represents an independent factor for inappropriate chronic oxidative stress and inflammatory factor surges during the healthy adulthood [37].

Browning values which express formation of brown pigments are shown in Tab. 3. As can be observed, slight formation of brown polymers MRP (melanoidins) took place during the baking of ginger cakes. The comparison of furosine, FAST index and browning data suggests that the Maillard reaction induced by baking conditions has progressed up to the formation of brown polymer precursors (fluorescent AGE) as the main product, accompanied by an extensive generation of early products (Amadori compounds indirectly measured as furosine).

Correlation study

In this study, results of antioxidant capacity of ginger cakes from the voltammetric experiments correlated with increased levels of extractable phenolics ($r = 0.93$). The antioxidant capacity of ginger cakes was negatively correlated with furosine content ($r = -0.95$), whilst it was highly positively correlated with FAST index ($r = 0.76$) and browning ($r = 0.47$). Taking into account the correlation between protein and furosine ($r = 0.99$), FAST index ($r = -0.94$) and browning data ($r = -0.67$) suggest that free fluorescent intermediary compounds and brown MRP may contribute to the antioxidant capacities of the samples. However, further work should be done in order to identify and characterize the antioxidative activity of these compounds potentially responsible for the ob-

served increase in antioxidant capacity of ginger cakes after baking. Previous studies also suggested the role of the advanced MRP as antioxidants discarding the antioxidant power of early MRP [27]. The relationship between protein and MRP contents in ginger cakes indicates that glycation of protein involves the formation of reducing structures and then supports their feasibility to assess protein quality of ginger cakes. Among the chemical indicators studied here, furosine and FAST index seem to be more appropriate than browning for assessing ginger cake protein quality.

CONCLUSIONS

The formulation and baking conditions affected extractable phenolics and antioxidant capacity of ginger cakes made following traditional and new recipes. Traditional ginger cakes made by employing dark and brown rye flours showed higher antioxidant capacities. The new formulation facilitated obtaining a product with lower antioxidant capacity but with better protein quality, being potentially healthier due to the lower content of advanced Maillard reaction products. Further investigation is needed in order to identify neo-antioxidants formed during cake-making and their contribution to the antioxidant capacity of the cakes. According to the data presented, advanced Maillard reaction products may be mainly responsible for the overall antioxidant activity of the baked ginger cakes. Based on the higher protein quality and chemical composition hereby analysed, ginger cakes formulated following new recipes should be preferred with the aim to lower the intake of dietary advanced Maillard reaction products from these widely consumed cakes.

Acknowledgements

This research was supported by project CSIC-Polish Academy of Sciences (2008PL0025).

REFERENCES

1. Michalska, A. – Ceglińska, A. – Zieliński, H.: Bioactive compounds in rye flours with different extraction rates. *European Food Research and Technology*, 225, 2007, pp. 545–551.
2. Mancini-Filho, J. – Van-Koij, A. – Mancini, D. A. P. – Cozzolono, F. F. – Torres, R. P.: Antioxidant activity of cinnamon (*Cinnamomum zeylancum*, Breyne) extracts. *Bollettino Chimico Farmaceutico*, 137, 1998, pp. 443–447.
3. Kikuzaki, H. – Nakatani, N.: Antioxidant effects of

- some ginger constituents. *Journal of Food Science*, *58*, 1993, pp. 1407–1410.
4. Frankel, S. – Robinson, G. E. – Berenbaum, M. R.: Antioxidant content and correlated characteristic of 14 monofloral honeys. *Journal of Apicultural Research*, *37*, 1998, pp. 27–31.
 5. Gheldof, N. – Engeseth, N. J.: Antioxidant capacity of honeys from various floral sources based on the determination of oxygen radical absorbance capacity and inhibition of in vitro lipoprotein oxidation in human serum samples. *Journal of Agricultural and Food Chemistry*, *50*, 2002, pp. 3050–3055.
 6. Mesa, M. D. – Silvan, J. M. – Olza, J. – Gil, A. – del Castillo, M. D.: Antioxidant properties of soy protein-fructooligosaccharide glycation systems and its hydrolyzates. *Food Research International*, *41*, 2008, pp. 606–615.
 7. Surai, P. F. – Sparks, N. H. C.: Designer eggs: from improvement of egg composition to functional food. *Trends in Food Science and Technology*, *12*, 2001, pp. 7–16.
 8. Lu, C. L. – Baker, R. C.: Characteristics of egg phosphovitin as an antioxidant for inhibiting, metal-catalyzed phospholipids oxidations. *Poultry Science*, *65*, 1986, pp. 2065–2070.
 9. Kroh, L. W.: Caramelisation in food and beverages. *Food Chemistry*, *51*, 1994, pp. 373–379.
 10. Wagner, K. H. – Derkits, S. – Herr, M. – Schin, W. – Elmadfa, I.: Antioxidative potential of melanoidins isolated from a roasted glucose-glycine model. *Food Chemistry*, *78*, 2002, pp. 375–382.
 11. Michalska, A. – Amigo-Benavent, M. – Zieliński, H. – del Castillo, M. D.: Effect of baking on the formation of MRPs contributing to the overall antioxidant activity of rye bread. *Journal of Cereal Science*, *48*, 2008, pp. 123–132.
 12. Hedegaard, R. V. – Granby, K. – Frandsen, H. – Thygesen, J. – Skibsted, L. H.: Acrylamide in bread. Effect of prooxidants and antioxidants. *European Food Research and Technology*, *227*, 2008, pp. 519–525.
 13. Hansen, A. – Schiberle, P.: Generation of aroma compounds during sourdough fermentation: applied and fundamental aspects. *Trends in Food Science and Technology*, *16*, 2005, pp. 85–94.
 14. Nguyen, C. H.: Toxicity of the AGEs generated from the Maillard reaction: on the relationship of food-AGEs and biological-AGEs. *Molecular Nutrition and Food Research*, *50*, 2006, pp. 1140–1149.
 15. Singleton, V. L. – Orthofer, R. – Lamuela-Raventos, R. M.: Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. *Methods in Enzymology*, *299*, 1999, pp. 152–178.
 16. Zielińska, D. – Szawara-Nowak, D. – Zieliński, H.: Comparison of spectrophotometric and electrochemical methods for the evaluation of antioxidant capacity of buckwheat products after hydrothermal treatment. *Journal of Agricultural and Food Chemistry*, *55*, 2007, pp. 6124–6131.
 17. Resmini, P. – Pellegrino, L. – Batelli, G.: Accurate quantification of furosine in milk and dairy products by direct HPLC method. *Italian Journal of Food Science*, *2*, 1990, pp. 173–183.
 18. Delgado-Andrade, C. – Rufian-Henares, J. A. – Morales, J. F.: Fast method to determine furosine in breakfast cereals by capillary zone electrophoresis. *European Food Research and Technology*, *221*, 2005, pp. 707–711.
 19. AOAC Official Method 979.09. Protein in grains. In: *Official Methods of Analysis*, Washington, D.C. : Association of Official Analytical Chemists, 2000, pp. 30–34.
 20. Birlouez-Aragon, I. – Leclere, J. – Quedraogo, C. L. – Birlouez, E. – Grongnet, J.-F.: The FAST method, a rapid approach of the nutritional quality of heat-treated foods. *Nahrung/Food*, *45*, 2001, pp. 201–205.
 21. Del Castillo, M. D. – Ames, J. M. – Gordon, M. H.: Effect of roasting on the antioxidant activity of coffee brews. *Journal of Agricultural and Food Chemistry*, *50*, 2002, pp. 3698–3703.
 22. Zieliński, H. – Michalska, A. – Ceglińska, A. – Lamparski, G.: Antioxidant properties and sensory quality of traditional rye bread as affected by the incorporation of flour with different extraction rates in the formulation. *European Food Research and Technology*, *226*, 2008, pp. 671–680.
 23. Andreassen, M. F. – Christensen, L. P. – Meyer, A. S. – Hansen, A.: Content of phenolic acids and ferulic acid dehydromers in 17 rye (*Secale cereale* L.) varieties. *Journal of Agricultural and Food Chemistry*, *48*, 2000, pp. 2837–2842.
 24. Woffenden, H. M. – Ames, J. M. – Chandra, S.: Relationships between antioxidant activity, color, and flavor compounds of crystal malt extracts. *Journal of Agricultural and Food Chemistry*, *49*, 2001, pp. 5524–5530.
 25. Rizzi, G. P.: Electrochemical study of the Maillard reaction. *Journal of Agricultural and Food Chemistry*, *51*, 2003, pp. 1728–1731.
 26. Lindenmeier, M. – Hofmann, T.: Influence of baking conditions and precursor supplementation on the amounts of the antioxidant pronyl-L-lysine in bakery products. *Journal of Agricultural and Food Chemistry*, *52*, 2004, pp. 350–354.
 27. Moreno, F. J. – Corzo-Marinez, M. – del Castillo, M. D. – Villamiel, M.: Changes in antioxidant activity of dehydrated onion and garlic during storage. *Food Research International*, *39*, 2006, pp. 891–897.
 28. Caboni, M. F. – Boselli, E. – Messia, M. C. – Velasco, V. – Fratianni, A. – Panfilli, G. – Marconi, E.: Effect of processing and storage on the chemical quality markers of spray-dried egg. *Food Chemistry*, *92*, 2005, pp. 293–303.
 29. Boctor, A. M. – Harper, A. E.: Measurement of available lysine in heated and unheated foodstuffs by chemical and biological methods. *Journal of Nutrition*, *94*, 1968, pp. 289–296.
 30. Erbersdobler, H. F. – Somoza, V.: Forty years of furosine – Forty years of using Maillard reaction products as indicators of the nutritional quality of foods. *Molecular Nutrition and Food Research*, *51*, 2007, pp. 423–430.

31. Hidalgo, A. – Rossi, M. – Pompei, C.: Estimation of equivalent egg age through furosine analysis. *Food Chemistry*, 94, 2006, pp. 608–612.
32. Hidalgo, A. – Rossi, M. – Pompei, C.: Furosine as a freshness parameter of Stell eggs. *Journal of Agricultural and Food Chemistry*, 43, 1995, pp. 1673–1677.
33. Garcia-Banos, J. L. – Corzo, N. – Sanz, M. L. – Olano, A.: Maltulose and furosine as indicators of quality of pasta products. *Food Chemistry*, 88, 2004, pp. 35–38.
34. Rada-Mendoza, M. – Garcia-Banos, J. L. – Villamiel, M. – Olano, A.: Study on nonenzymatic browning in cookies, crackers and breakfast cereals by maltulose and furosine determination. *Journal of Cereal Science*, 39, 2004, pp. 167–173.
35. Del Castillo, M. D. – Sanz, M. L. – Vicente-Arana, M. J. – Corzo, N.: Study of 2-furoylmethyl amino acids in processed foods by HPLC-mass spectrometry. *Food Chemistry*, 79, 2002, pp. 261–266.
36. Matiacevich, S. B. – Buera, M. P.: A critical evaluation of fluorescence as a potential marker for the Maillard reaction. *Food Chemistry*, 95, 2006, pp. 423–430.
37. Silvan, J. M. – Van de Lagemaat, J. – Olano, A. – del Castillo, M. D.: Analysis and biological properties of amino acid derivatives formed by Maillard reaction in foods. *Journal of Pharmaceutical and Biomedical Analysis*, 41, 2006, pp. 1543–1551.

Received 28 May 2010; revised 9 July 2010; accepted 16 August 2010.